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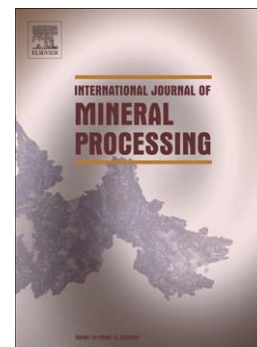
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## Utilisation of residue Gas Sludge (BOS sludge) for removal of heavy metals from Acid Mine Drainage (AMD)

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### Abstract

This investigation employed waste gas sludge (BOS sludge) which is an end-waste from steelmaking process as a novel adsorbent to study adsorption phenomena on real acid mine drainage. BOS sludge was used to treat Wheal Jane Mine (Cornwall, UK) AMD in this work. Batch experiments were conducted as function of initial solution pH, adsorbent loading, regeneration and thermal treatment to study the performance of BOS sludge in removing manganese, copper, iron, and zinc.

Kinetic studies indicated that the rate of adsorption of the heavy metals by BOS sludge was rapid. A high pH promoted adsorption and removal of the heavy metal ions was not only due to ion exchange or adsorption but also partly due to co-precipitation effect. The treatment of Wheal Jane mine AMD demonstrated that about 100% of Cu and Fe, 97% of Zn and 94% of Mn were removed from solution. The results show that BOS sludge has great potential as an alternative material in the treatment of real waste water streams. Thus BOS sludge could be used as a sustainable sorbent for the more expensive materials in AMD treatment technologies due to its adsorptive properties, high availability, large quantities and low cost.

**Keywords:** Heavy metals; Acid mine drainage (AMD); BOS sludge; Adsorption.

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## 1.0 Introduction

Acid Mine Drainage (AMD) is an environmental pollutant resulting from a combination of weathering and mining activities. Acid mine waters have low pH-values and high concentrations of toxic and heavy metal contaminants ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ) which are not biodegradable and thus tend to accumulate in the environment causing various threats in nature (Skousen and Ziemkiewicz, 1996; McGinness et al., 1999; Skousen et al., 2000).

Britain has a long history of mining for coal, metal ores and other minerals. The number of mines is enormous, reports suggest in Wales, the South West and Northumbria over 3,700 sites exist. No significant metal mines are still in use; the last large tin mine in Cornwall closed in 1998. Monitoring and studies have shown that a large number of abandoned metal mines are significant contributors to heavy metal and toxic pollution into rivers and seas (Environment Agency, 2008).

There are a number of Acid Mine Drainage (AMD) treatment technologies and these fall into two broad categories, passive and active treatments. However conventional methods such as lime based chemical precipitation, ion exchange and other processes have a number of shortcomings; which are extensive land utilisation, production of large secondary solid waste, high capital and operating costs. Overall, AMD treatment processes depend highly upon many factors; for example type and concentrations of the dissolved metal ions in AMD solutions.

Adsorption is becoming a popular method for the removal of heavy metals from the AMD (Omer et al., 2003). Natural materials, waste and residue products from industrial or agricultural activities have excellent potential as an economic adsorbent for heavy metal removal from AMD solution. It is believed that such materials may be considered as alternative adsorbents to activated carbons and ion exchange resins (Ahmaruzzaman et al., 2011; Bailey et al., 1999; Barakat et al., 2011; Kurniawan et al., 2006; Sud et al., 2008).

High metal adsorption capacity and efficiency involving steel slags in single and binary adsorbate systems have been investigated, and the mechanisms of adsorption and the effects of variables on metal adsorption have also been assessed. For silicate based materials such as slags, many authors

believe metal adsorption process to occur through ion exchange and metal hydroxide/silicate precipitation (Dushina and Aleskovski, 1976), physical adsorption based on ion exchange (Lopez et al., 1995), primarily sorption through ion exchange and some form of metal silicate precipitation (Dimitrova & Mehanjiev, 1998). However the studies are limited, inconsistent and the adsorption mechanisms are yet to be understood fully in detail.

Integrated steel plants generate large amounts of different solid wastes such as blast furnace slag, steel slag, mill scales and many others. The fine solid particles recovered after wet scrubbing of the gas generated from basic oxygen furnace (BOF/BOS) in the sludge form are known as waste gas sludge (BOS sludge). A newer approach of utilising this waste material (BOS sludge) deserves attention as a potential and alternative solution to recycling routes.

BOS sludge has not previously been studied or examined under adsorption purposes for acid mine drainage treatment, hence very limited literature and data are available on this particular material. However due to its adsorptive properties, presence of exchangeable cations (neutralising potential ability) and its high availability, BOS sludge can be considered as a novel adsorbent for the removal of heavy metal ions. Thus employing BOS sludge in an efficient and cost effective manner would solve two environmental problems simultaneously.

However there are a number of challenges, two major restrictions associated with BOS sludge usage could be that the sorbent must remain submerged during treatment. The BOS sludge will harden into a concrete-like substance, thus leading to reduced surface area and porosity. Another challenge could be the disposal of used BOS sludge (spent sorbent) which was not dealt with in this particular study and this could be a potential area of further study which could ultimately may result in increase of environmental concerns associated with AMD treatment. Before this technology is implemented on an industrial scale, the construction of an optimised pilot plant using BOS sludge to treat different real AMD solutions would be a constructive plan forward, as this could generate more options on how to treat the spent sorbent with different solvents prior to discharge. Further research and investigations must be carried out in order to determine different operating conditions and flow regimes which simulate real plant operation and to assess the longevity of the treatment.

This study investigated the adsorption efficiency and removal rates of copper, iron, zinc and manganese ions using waste gas sludge (BOS sludge; as received). The aim of this present work is to assess the effectiveness of BOS sludge as a sorbent in treating AMD solutions from Wheal Jane disused mine (Cornwall, UK).

## **2.0 Materials and Methods**

### **2.1 Adsorbent and adsorbate**

In this study BOS sludge samples from Tata Steel plant in Port Talbot (South Wales) were used, provided by Harsco metals & mineral Ltd, UK. The samples were used in their natural state (“as received”) with no chemical modifications, unless stated. The particle size distribution of the samples was determined using screens and a sieve shaker.

The particle size range of the BOS sludge used in this study was +1mm,-1.4mm. Real AMD from Wheal Jane mine was collected in sealed containers. Concentrations of copper, iron, manganese and zinc were determined by the atomic absorption spectrometer (AAS).

The results presented in Table 1 show the oxide composition of BOS sludge as determined by XRF. The high lime (13.1% CaO) content means that the material has a potentially high neutralising capacity for acidic effluents. The other characteristics of BOS sludge that were investigated are also listed in Table 1.

The density of BOS sludge was determined using a helium gas PYCNOMETER from Micrometrics, model AccuPyc II 1340. The porosity of BOS sludge samples were measured using a mercury porosimeter. Surface area measurements were also determined by Nitrogen adsorption fitted to the BET equation (Brunauer, 1943), using the TRISTAR 3000 apparatus from Micrometrics.

### **2.2 Batch Sorption studies**

Batch adsorption tests/studies provide information on adsorption equilibrium characteristics and adsorption kinetics, which are important in determining the effectiveness of the adsorbent in removing solute from solution. Specified masses of BOS sludge samples were mixed with 200 ml

solution of Wheal Jane AMD for a predetermined time period and agitated over tumbling mill at 110 rpm. The initial concentrations of copper, iron, zinc and manganese in AMD from Wheal Jane mine collected were 1.1, 74, 23 and 4 mg/l respectively and these were measured using the AAS. The pH of Wheal Jane water was in a range of about 2.7- 2.9  $\pm$  0.1. The final concentrations of the heavy metal ions in the aqueous phase were determined using AAS from which efficiency and adsorption capacities for each sample was calculated.

The percent adsorption (%) was calculated using the equations:

$$\% \text{ Adsorption} = (C_i - C_f) / C_i \times 100, \quad [1]$$

Where,  $C_i$  and  $C_f$  are the concentrations of the metal ions in the initial and final solutions respectively.

The amount of metal adsorbed from aqueous solution at time  $t$ , was determined by the following equation:

$$q_t = m_s/m = (C_o - C_t)(V/m), \quad [2]$$

Where  $q_e$  is the amount of heavy metal ions adsorbed at any time, mg/g adsorbent;  $m_s$  is the mass of metal adsorbed, mg;  $m$  is the adsorbent mass, g;  $C_o$  is the initial concentration of heavy metal ions, mg/l;  $C_t$  is the liquid- phase concentration of heavy metal ions at any time, mg/l;  $V$  is the volume of solution from which adsorption occurs, L.

The equilibrium amount of metal adsorbed from aqueous solution was determined by the following equation:

$$q_e = m_s/m = (C_o - C_e)(V/m), \quad [3]$$

Where  $q_e$  is the amount of heavy metal ions adsorbed at equilibrium, mg/g adsorbent;  $m_s$  is the mass of metal adsorbed, mg;  $m$  is the adsorbent mass, g;  $C_o$  is the initial concentration of heavy metal ions, mg/l;  $C_e$  is the liquid- phase concentration of heavy metal ions at equilibrium, mg/l;  $V$  is the volume of solution from which adsorption occurs, L.

### **2.2.1 Effect of adsorbent dosage on adsorption process**

Different masses were used in this study, ranging from 8g, 16g and 24 g of BOS sludge and these were contacted with Wheal Jane solution. The mixture was agitated and the samples were taken at regular intervals for AAS analysis.

### **2.2.2 Effect of initial solution pH on adsorption process**

Wheal Jane AMD solution was contacted with 24g of BOS sludge sample and the solution pH was varied using NaOH from the initial pH (2.8) to 3.5 and 4.5 to investigate the influence of pH variation in relation to removal of heavy metals. The pH of each sample was measured using a Microprocessor pH meter (Hanna PH211).

### **2.2.3 Effect of heat treatment on adsorption process**

A furnace used for heating BOS sludge at 200°C for 60 minutes in an air atmosphere; 24 g of thermally treated BOS sludge was contacted with Wheal Jane AMD solution for 180 minutes; the mixture was agitated and samples were collected at regular intervals and analysed.

### **2.2.4 Regeneration processing of BOS sludge**

200ml of Wheal Jane solution was contacted with 24 g of BOS sludge for 180 minutes; samples filtered and the BOS separately contacted with NaCl and H<sub>2</sub>SO<sub>4</sub> for 20 minutes. The regenerated sample was contacted again with 200 ml of Wheal Jane AMD for 180 minutes under the same agitation condition and the samples were collected at regular intervals and analysed. Sulphuric acid concentration used was 2 % (wt). Sodium chloride (NaCl) solution, 20 mg/l was also prepared and used in desorption and regeneration tests.

## **3.0 Results and Discussion**

### **3.1 Effect of adsorbent dosage on adsorption process**

The amounts of metal adsorbed versus time are shown in Figure 1-4. For 24g sample, the adsorption of all metal ions displayed a similar trend to one another. For all the ions, adsorption is



steep for the first 15 min, after which for all respective metals the adsorption levels off as equilibrium is attained. Percent adsorption of 100%, 100%, 97.9%, and 94.8% for copper, iron, zinc and manganese respectively were achieved for 24g sample.

In terms of the percentage of heavy metals adsorbed from solution, it is evident that an increase in BOS sludge mass resulted in an increase in the adsorption of the heavy metals just for iron, zinc and manganese, Table 2. Results show the amount of metal adsorbed ( $q_e$ ) at equilibrium is lower as the mass of the samples increased. This is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added. Hence the amount of metal adsorbed from AMD water per unit mass of samples at equilibrium is moderately lower.

Figure 1 shows that the rate of metal removal is initially instant and progressive, that is within the first 15min. The kinetics of the neutralisation reaction is rapid as the pH increased through the sorption period, Figure 2. After the initial period slower adsorption may be due to slower diffusion or the build-up of passive layers. This effective removal can also be a result of the interactions of heavy metals with the adsorption sites on the surface of BOS, which can easily be accessed by the diffusing heavy metals. However the effect of precipitation of metal hydroxides must not be ruled out. The order of adsorption from Wheal Jane AMD was found to be: copper $\geq$ iron>zinc>manganese.

The Wheal Jane mine water maximum consent limit for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5mg/l respectively (Bone, 2003; United Kingdom). Results from Table 2 prove that BOS sludge is capable of treating real AMD as the final concentrations of four heavy metals ( $C_e$ ) meet the maximum Wheal Jane consent limit requirement.

Higher adsorbent dosage promoted a better efficiency in the removal of heavy metal ions. As the final heavy metal concentration for 24g sample of BOS sludge show that BOS sludge was able to treat copper, iron and zinc within the Environmental Quality Standard (EQS), Table 2. Hence it is recommended that BOS sludge can effectively be used to treat real AMD.

### 3.2 Effect of pH trend on the adsorption process

From chemical analysis of BOS sludge and observed high pH values, it is possible that ion exchange process, adsorption and precipitation may be the major mechanisms involved as proposed in several studies (Dimitrova et al., 1996; Dimitrova and Mehandgiev, 2000; Feng et al., 2004; Manchisi et al., 2013; Kim et al., 2008). pH increases as mass of the adsorbent increases and this is shown in Figure 5. This is in agreement with various researchers including (Kim et al., 2008; Manchisi et al., 2013, Zhou and Haynes, 2010, Chen et al., 2011) whom have also identified BF/steel slags as a suitable candidate to remediate waters contaminated by acid mine drainage, since such materials proved to have a significant acid neutralising potential that can be exploited to precipitate out a majority of dissolved metals by increasing solution pH.

The high pH obtained (value of 9.93) is also due to the dissolution of the BOS sludge during the agitation; exposing high number active adsorption sites. More copper and iron were adsorbed from solution in comparison to the other metals (Mn, Zn). Increasing the pH of AMD water to the desired value causes metal precipitation in the form of hydroxides.

The sorption becomes complicated in real AMD because of the ratios of heavy metals to one another resulting in solute-solute competitions and the solute-surface interactions. This indicates that besides chemisorption, ion exchange and precipitation some other complex mechanisms are predominantly involved. Thus, the way that AMD is treated highly depends on the type and concentrations of the metal cations and also the anions present in water.

### **3.3 Effect of initial solution pH on adsorption process**

One of the methods of acid mine water treatment is chemical precipitation, which is related to increase of AMD pH (Plasari and Muhr, 2007). The pH required to precipitate most metals from AMD water ranges from pH 6 to 9 (except  $\text{Fe}^{+3}$ , which precipitates at  $\text{pH} > 3.5$ ) (Skousen et al., 2000). Increasing the pH of AMD water can lead to metal precipitation in the form of hydroxides and the interaction among the metals in AMD water can effectively influence the reaction rate and oxidation state of the metals during contact with adsorbents or solvents.

For instance, manganese will be simultaneously co-precipitated with Fe precipitation from water at pH 8, only if the concentration of iron in the water is much greater than the manganese content

(Sheremata and Kuyucak, 1996). This finding that in the presence of a large excess of Fe the Mn is precipitated at pH 8 may be confirmed in this study, as at pH 8 (89.1%) of manganese was recovered, Figure 3.

In oxygen-poor AMD iron is mainly as  $\text{Fe}^{2+}$ , which should be precipitated at pH 8 according to literature (Xinchao et al., 2005). In this study at pH 8 (95.4%) was recovered from solution as shown in Figure 6. The reason for the iron precipitation across the studied range may also be progressive oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which iron precipitates in the form of  $\text{Fe}(\text{OH})_3$ , which starts at  $\text{pH} > 3.5$ . More iron is recovered when solution pH increased to 4.5 (98.5%) compared to pH 2.8 (95.4%), Figure 8 and Figure 6. According to literature zinc is precipitated in the range pH 5.5 to 7 in acid mine drainage (Sheremata and Kuyucak, 1996). In Figure 6 at pH 9.9, 94% of zinc is recovered from the solution.

In another study, real AMD solution similar to Wheal Jane mine (non-coal mines) was neutralised by NaOH (0.5 mol/L) as a precipitating reagent. Results reported that AMD neutralisation with NaOH to the pH of 8.2 was achieved which removed 92.3 % of copper, 93.3% of zinc, 96.6 % of iron and 15.9 % of manganese (Balintova and Petrlikova, 2007). Overall the efficiency of metal adsorption depends on solution pH trend and sorbent type (its physical properties); this is also in agreement with results obtained by Moreno et al., 2001 and Alvarez-Ayuso et al., (2003) whom used inorganic sorbents (zeolites) for purification of acid mine waters.

### 3.4 Effect of heat treatment on adsorption process

Figure 9-12, show how heat/thermal pre-treatment of the BOS sludge affects its efficiency in heavy metal ion adsorption, adsorption rate increased with time, but to a limit. The rate of adsorption of all heavy metal ions were reduced when thermally pre-treated BOS sludge was used, copper and manganese adsorption rates were reduced significantly, 26.3% for copper and 9.8% for manganese as shown in Figure 9 and Figure 12 respectively.

The physical properties of untreated BOS comply with a greater uptake of this sample rather than those of thermally pre-treated sample. Surface area measurements for thermal pre-treated BOS were determined by Nitrogen adsorption fitted to the BET equation (Brunauer 1943). The samples that

were exposed to thermal condition had reduction in surface area ( $12.92 \text{ m}^2\text{g}^{-1}$ ) resulting in a lower total pore area (porosity 66.29%); this is because of thermal runaway, while the BOS structure collapses the porosity of BOS also decreases and hence the adsorption capacity is reduced. This is also observed in the difference in pH obtained through the sorption as untreated BOS sludge sample depicts higher pH, which in turn promotes higher removal rates of all metals, as shown Figure 13.

Moreover, after thermally treating BOS its colour changed slightly; this may be an indication of a change in structure and/or composition of the BOS sludge. The difference in the amount removed from solution by the two samples was substantial to justify the use of untreated BOS sludge, since pre-treatment increases the cost of AMD treatment in practice.

### 3.5 Regeneration processing of BOS sludge

A good adsorbent must have a high adsorption capacity, but also needs to exhibit good regeneration for multiple usages (Richardson et al., 2002). Desorption of heavy metal ions from an adsorbent or the regeneration of an adsorbent is of great practical importance. This is one of the characteristics which is considered in choosing an adsorbent for any practical application (Richardson et al., 2002). Two adsorption – desorption cycles were performed for all 4 heavy metal ions. The effect of regeneration on adsorption capacity is presented in Table 3. For copper and manganese, there was an observable drop in the adsorption capacity of BOS sludge regenerated using NaCl; despite the high concentration of sulphuric acid it was in favour of iron uptake in comparison to manganese and zinc. Desorption takes place because of the displacement of the heavy metal ions from adsorption sites on the BOS sludge structure by either  $\text{H}^+$  ions, in the case of acid or  $\text{Na}^+$  ions from NaCl solution. This process is mainly driven by the concentration driving force, which favours  $\text{H}^+$  and  $\text{Na}^+$  ion adsorption because of the high solution concentrations used.

According to Table 3, it is evident that neither of regenerating agents performed as anticipated. The desorption series follow this order: iron>zinc>manganese>copper and adsorption series follow this trend: Copper=iron>zinc>manganese. There is an observable drop in the adsorption capacity of BOS sludge that has been regenerated using sulphuric acid. The adsorption capacity of regenerated BOS sludge dropped, since there was a decrease in adsorption capacity from cycle 1 to 2; this is probably because of acid resulting in neutralisation of much of alkalinity present in BOS sludge.

This drop in capacity may also be due to the possible destruction and distortion of the BOS sludge structure by acid dissolution. Zhou and Haynes (2010) also found that sorption capacity of blast furnace and steel slags on removal of heavy metals such as of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{3+}$  from aqueous solution also decreased appreciably, hence it was evident that acid is not a suitable reagent for regeneration of blast furnace or steel slags.

Some other reagents, such as the metal complexing agent EDTA might however be appropriate (Santona et al. 2006). The effectiveness of different regenerating solutions such as  $\text{NaNO}_3$ ,  $\text{HCl}$ ,  $\text{CaCl}_2$  at different concentrations could also be investigated if regeneration is considered to be an option. The adsorption capacity of BOS sludge regenerated using  $\text{NaCl}$  was also reduced. Therefore, regenerated BOS sludge cannot effectively meet the maximum Wheal Jane consent limit thus insuring that regenerated BOS sludge can handle only relatively dilute AMD solutions or preferably downstream to another treatment process.

#### 4.0 Conclusion

Kinetic studies indicated that the rate of adsorption of the heavy metals by BOS sludge was rapid for the first 15 minutes and then gradually decreased. About 100%, 100%, 97% and 94% of copper, iron, zinc and manganese respectively were adsorbed from Wheal Jane AMD solution. Removal of the heavy metal ions was not probably only due to ion exchange or adsorption but also due to co-precipitation.

There were a number of operational conditions which were found to influence and increase the rate of metal uptake by BOS; these include an increase in adsorbent dosage; an increase in initial solution pH and for thermal treatment of BOS prior to adsorption, the results showed that thermally treated BOS sludge did not enhance the capacity and efficiency of BOS sludge in treating AMD water.

In this study a waste by-product was used as an adsorbent with the main aim of maximum utilisation, hence regeneration of this material may not be process priority. However the adsorption capacity of regenerated BOS sludge reduced, since there was a drop in the adsorption rates through regeneration cycles. Thus, regenerated BOS sludge cannot effectively meet the maximum Wheal

Jane consent limit thus insuring that regenerated BOS sludge can handle only relatively dilute AMD solutions.

The results indicate that BOS sludge known as a waste from steelmaking process can be used as a novel and functional substitute for the more expensive sorbents that are currently being used in AMD treatment technologies. Although results show BOS sludge can be used effectively for the removal of heavy metal ions from real acidic solutions, however further research and development needs to be conducted with various real AMD solutions in order to understand the adsorption mechanisms furthermore.

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### Reference

- Ahmaruzzaman, M. 2011. Industrial Wastes as Low-Cost Potential Adsorbents for the Treatment of Wastewater Laden with Heavy Metals. *Advances in Colloid and Interface Science*, 166 [1-2], 36-59.
- Alvarez-Ayuso, E., Garcia-Sanchez, A., Querol, X., 2003. Purification of metal electroplating waste waters using zeolites. *Water Research*, 37, 4855-4862.
- Bailey, S. E., Olin, T. J., Bricka, R. M., Adrian, O. A., 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33[11], 2469-2479.
- Balintova, M., and Petrilkova, A. 2007. Study of pH influence on the selective precipitation of heavy metals from acid mine drainage. *Chemical Engineering Transactions*, 25, 345-350.
- Barakat, M. A. 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4, 361-377.
- Bone, B., 2003. Remediation scheme to mitigate the impacts of abandoned mines. Environmental Agency for England and Wales [Available at: [http://www.cluin.org/romania/presentations/natoccms\\_uk\\_cases.pdf](http://www.cluin.org/romania/presentations/natoccms_uk_cases.pdf):accessed 05/11/2010].
- Chen, X., Hou, W.H., Song, G.L., Wang, Q.H. 2011. Adsorption of Cu, Cd, Zn and Pb ions from aqueous solutions by electric arc furnace slag and the effects of pH and grain size. *Chem. Biochem. Eng.*, 25[1], 105-114.

- Dimitrova, S.V., Mehandgie, D.r., 1996. Lead removal from aqueous solutions by granulated blast furnace slag. *Construct Build Mater*, 1[3], 191-193.
- Dimitrova, S. V. and Mehanjiev, D. R., 1998. Lead Removal from Aqueous Solutions by Granulated Blast Furnace Slag. *Water Research*, 32[11], 3289-3292.
- Dimitrova, S.V., and Mehandgiev, D.R., 2000. Interaction of Blast-furnace slag with heavy metal ions in water solutions. *Water Research*. 34, 1957-1961.
- Dushina, A. and Aleskovski, V. 1976. Ion Exchange as First Stage of the Solid Substance Transformation into Electrolytic Solutions. *Journal of Applied Chemistry*, 49, 41-49.
- Environment Agency, 2008. Abandoned mines and the water environment; coal authority. [Available at: <http://cdn.environment-agency.gov.uk/scho0508bnzs-e-e.pdf>: last accessed on January 2013].
- Feng, D., van Deventer, J. S. J. and Aldrich, C. 2004. Removal of pollutants from acid mine wastewater using metallurgical by-product slags. *Separation and Purification Technology*, 40, 61-67.
- Kim, D.-H., Shin, M.-C., Choi, H.-D. 2008. Removal Mechanisms of Copper using Steel-Making Slag: Adsorption and Precipitation. *Desalination*, 223, 283-289.
- Kurniawan, T. A., Chan, G. Y. S., Lo, W. 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment*, 366, 409-426.
- Lopez, F. A., Perez, C., Sainz, E. 1995. Adsorption of  $Pb^{2+}$  on Blast Furnace Sludge. *Journal of Chemical Technology and Biotechnology*. 62 [2], 200-206.
- McGinness, S., 1999. Treatment of Acid Mine Drainage. Research Paper 99/10. House of Commons, London.
- Manchisi, J., Rowson, N.A., Simmons, M.J.H. 2013. Kinetics of Metals Adsorption in Acid Mine Drainage Treatment with Blast Furnace Slag. School of Chemical Engineering, University of Birmingham.
- Moreno, N., Querol, X., Ayora, C., 2001. Utilization of zeolites synthesised from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology*, 35, 3526-3534.
- Motsi, T., Rowson, N.A., Simmons, M.J.H., 2010. Adsorption of heavy metals from acid mine drainage (AMD), by natural Zeolite. The University of Birmingham, Thesis.
- Plasari E., and Muhr H.2007. Development in precipitation engineering for process intensification in the environmental protection and other purification industrial activities. *Chemical Engineering Transactions*, 11, 65-70.

Richardson, J.F., Harker, J.H., Backhurst, J.R., 2002. Coulson & Richardson's Chemical Engineering Volume 2, Fifth edition, Butterworth Heinemann.

Santona, L., Castaldi, P., Melis, P., 2006. Evaluation of the interaction mechanisms between red muds and heavy metals. *Journal of Hazardous Materials*, 136[2], 324-329.

Sheremata T., and Kuyucak N., 1996. Value recovery from acid mine drainage, MEND project 3.21.2a, Pointe-Claire, PQ, Noranda Technology Center. Pointe Claire, Quebec, Canada.

Skousen, J. and P., Ziemkiewicz. 1996. Acid Mine Drainage Control and Treatment. 2nd Ed. National Research Center for Coal and Energy, National Mine Land Reclamation Center, West Virginia University, Morgantown, pp. 362.

Skousen, J.G., Sexstone., A., Ziemkiewicz, P.F. 2000. Acid mine drainage control and treatment. Reclamation of Drastically Disturbed Lands. Chapter 6, pp.1-32.

Sud, D., Mahajan, G. and Kaur, M. P. (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresource Technology*, 99 6017-6027.

Xinchao W., Roger C., Viadero J. and Karen M., 2005. Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation. *Environ. Eng. Sci*, 22[6], 745-755.

Zhou, Y.-F.; Haynes, R. J. 2010. Sorption of heavy metals by inorganic and organic components of solid wastes: Significance to use of wastes as low-cost adsorbents and immobilizing agents. *Critical Reviews in Environmental Science and Technology*, 40[11], 909-977.

Zhou, Y.-F. and Haynes, R. J. 2010. A Comparison of Inorganic Solid Wastes as Adsorbents of Heavy Metal Cations in Aqueous Solution and Their Capacity for Desorption and Regeneration. *Water Air Soil Pollut*, 218, 457-470.



Table 1 Properties of untreated BOS sludge

Chemical Composition	Physical Properties		
Oxide	% w/w	Parameter	Value
FeO	23.95	Porosity (%)	74.2548
SiO <sub>2</sub>	2.60	Surface area; m <sup>2</sup> g <sup>-1</sup>	16.95
Al <sub>2</sub> O <sub>3</sub>	1.62	Surface area of thermally treated sample; m <sup>2</sup> g <sup>-1</sup>	12.92
H <sub>2</sub> O	12.9	Density; g/cm <sup>3</sup>	4.2693
MnO	1.41	Average pore dia. (μm)	1.665
CaO	13.11	Moisture content (%)	19.21
MgO	1.7	Physical form	Black slurry

Table 2 Effect of BOS sludge mass on the removal of heavy metals from Wheal Jane AMD solution at pH ~ 2.8; 20°C; total contact time 180min; particle size: (+1mm,-1.4mm).

Heavy metal ions	Adsorbent Mass (g)	Amount Adsorbed, q <sub>e</sub> (mg/g)	Final Concentration (mg/l)	Wheal Jane maximum consent limit (mg/l)	EQS limit (mg/l)
	8	0.0275	0		
<b>Copper</b>	16	0.0138	0	<b>0.08</b>	<b>0.028</b>
	24	0.0092	0		
	8	1.820	1.2		
<b>Iron</b>	16	0.916	0.71	<b>5.0</b>	<b>1.0</b>
	24	0.617	0		
	8	0.555	0.8		
<b>Zinc</b>	16	0.281	0.55	<b>2.5</b>	<b>0.5</b>
	24	0.188	0.49		
	8	0.085	0.6		
<b>Manganese</b>	16	0.043	0.53	<b>1.0</b>	<b>0.03</b>
	24	0.032	0.21		

Table 3: The percentage recovery of heavy metals from BOS sludge by regeneration. (24g of BOS; 200ml Wheal Jane solution; agitated over tumbling mill at 110rpm (contact time: 3 hours; particle size: +1mm,-1.4mm).

Heavy metals	% Recovered over cycle 1	% Recovered over cycle 2	% adsorption Untreated BOS sludge
<b>Copper</b>			
NaCl	66.31	44.75	<b>100</b>
H <sub>2</sub> SO <sub>4</sub>	42.10	11.22	
<b>Iron</b>			
NaCl	92.45	90.12	<b>100</b>
H <sub>2</sub> SO <sub>4</sub>	97.39	93.71	
<b>Zinc</b>			
NaCl	93.22	89.96	<b>97.87</b>
H <sub>2</sub> SO <sub>4</sub>	87.35	80.48	
<b>Manganese</b>			
NaCl	72.40	54.82	<b>94.75</b>
H <sub>2</sub> SO <sub>4</sub>	64.25	52.13	

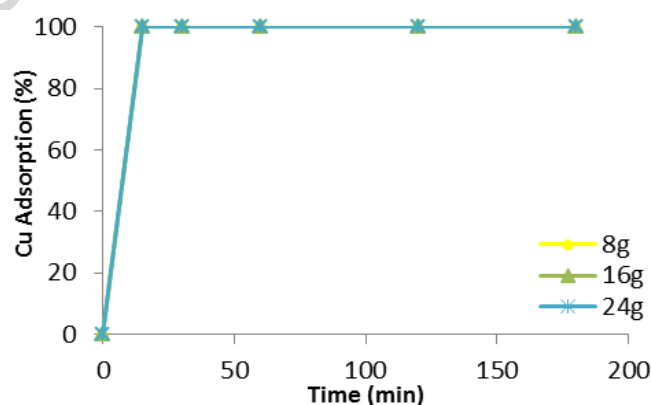


Fig. 1: The effect of mass of BOS sludge on the adsorption of Cu from Wheal Jane solution (particle size: +1mm,-1.4 mm; initial: pH~ 2.8).

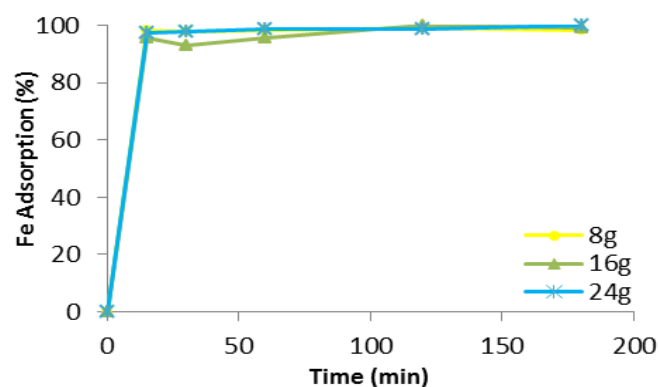


Fig. 2: The effect of mass of BOS sludge on the adsorption of Fe from Wheal Jane solution (particle size: +1mm,-1.4 mm; initial: pH~ 2.8).

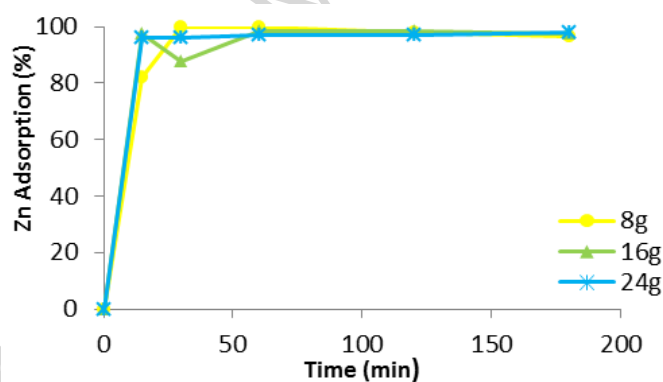


Fig. 3: The effect of mass of BOS sludge on the adsorption of Zn from Wheal Jane solution (particle size: +1mm,-1.4 mm; initial: pH~ 2.8).

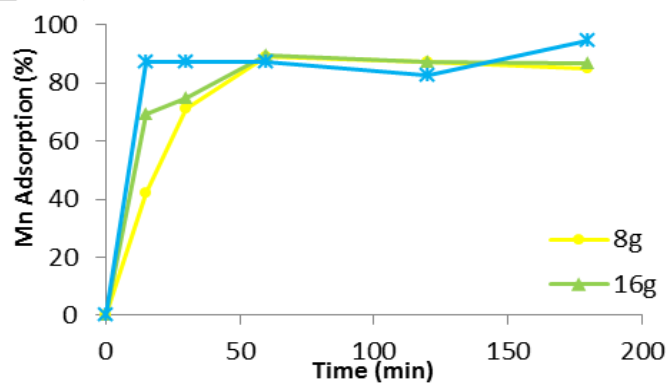


Fig. 4: The effect of mass of BOS sludge on the adsorption of Mn from Wheal Jane solution (particle size: +1mm,-1.4 mm; initial: pH~ 2.8).

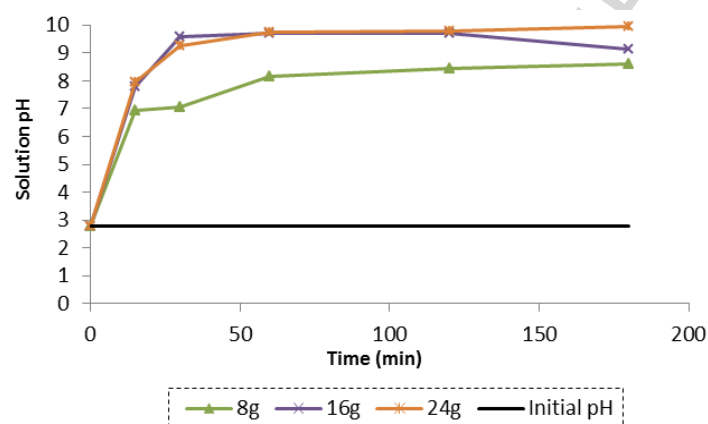


Fig. 5: Effect of BOS sludge mass vs. solution pH trend on the adsorption of heavy metals (copper, zinc, manganese, iron) from Wheal Jane AMD (200ml solution); particle size: +1mm,-1.4mm; initial pH~ 2.8.

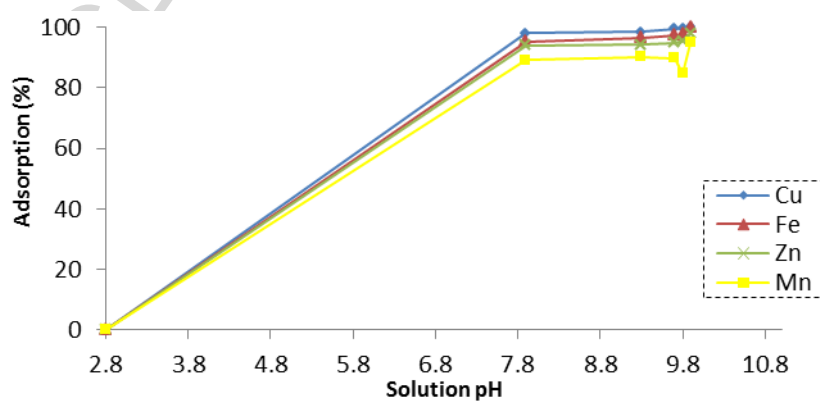


Fig. 6: Effect of initial pH (2.8) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).

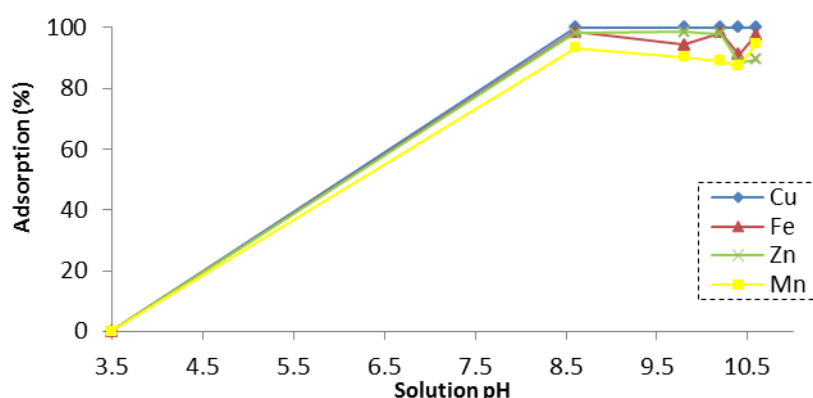


Fig. 7: Effect of initial pH (3.5) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).

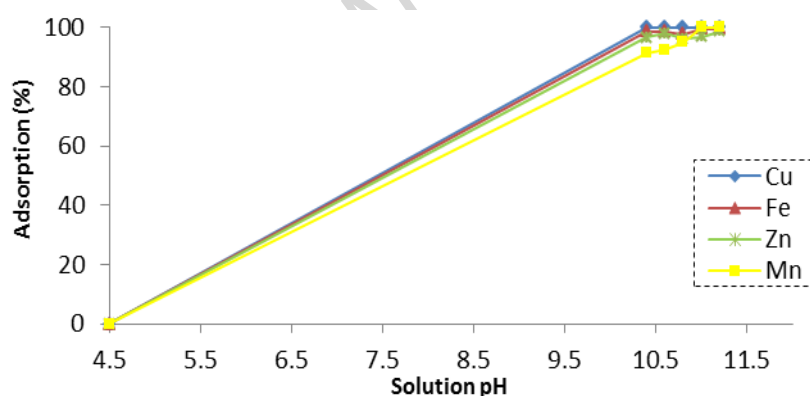


Fig. 8: Effect of initial pH (4.5) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).

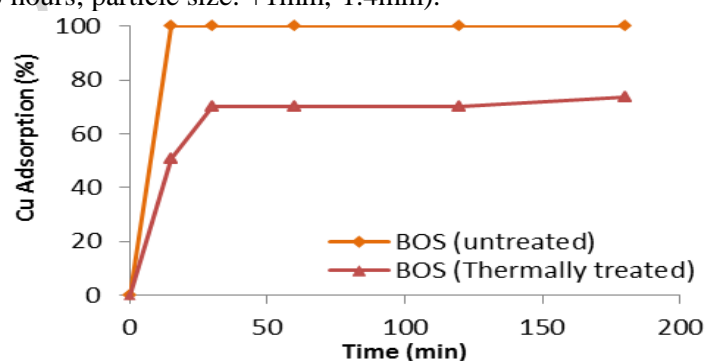


Fig. 9: Effect of thermally treated BOS sludge on its capacity to remove Cu ions from Wheal Jane mine AMD.

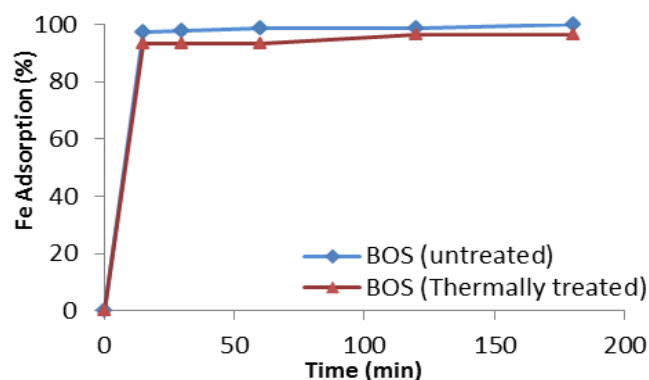


Fig. 10: Effect of thermally treated BOS sludge on its capacity to remove Fe ions from Wheal Jane mine AMD.

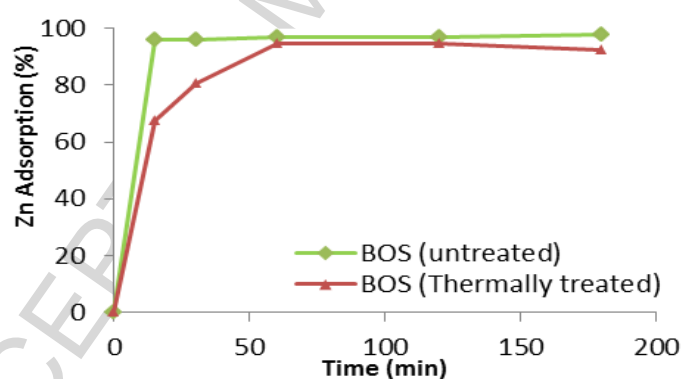


Fig. 11: Effect of thermally treated BOS sludge on its capacity to remove Zn ions from Wheal Jane mine AMD.

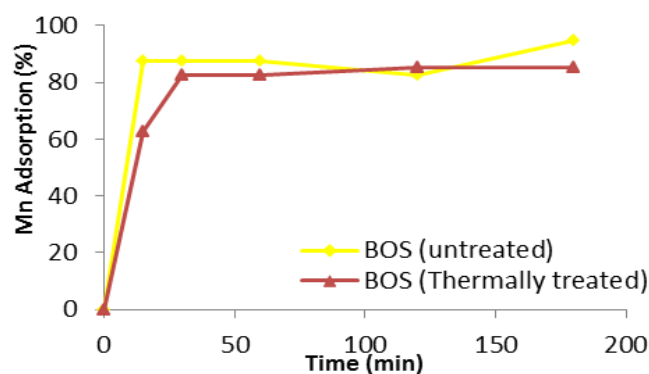


Fig. 12: Effect of thermally treated BOS sludge on its capacity to remove Mn ions from Wheal Jane mine AMD.

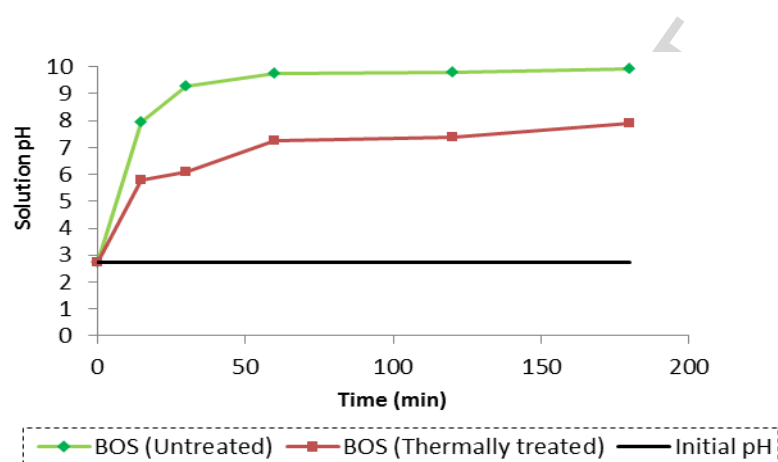


Fig.13: Comparison between thermally treated BOS sludge and untreated BOS in treating Wheal Jane AMD after 180 minutes.

## Highlights

- Batch mode kinetic studies were performed to assess the functionality of BOS sludge as a low cost sorbent for real AMD treatment.
- Results showed high pH obtained due to the dissolution of the BOS sludge (neutralising potential) during the agitation of AMD solution and BOS.
- Results revealed that the efficiency and adsorption rates were favoured with an increase in BOS mass and an increase in the initial solution pH.
- Residue Gas Sludge has the potential to function as an effective adsorbent in removal of heavy metal ions from real acid mine drainage solutions.